

F469

Claims

1. A process for trimerisation of olefins, which process includes the step of contacting an olefinic feedstream with a catalyst system which includes a transition metal compound and a heteroatomic ligand and wherein the trimer is an olefin and wherein the heteroatomic ligand is described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C and is selected to exclude $(CH_2)_xY(CH_2)_y$, where Y is $-P(R^6)-$, $-N(R^6)-$, $-As(R^6)-$, $-Sb(R^6)-$ or $-S-$ and x and y are individually 1-15 and wherein R^6 is hydrogen or a halogen or a nitro group or a hydrocarbyl or a substituted hydrocarbyl, and each R is independently selected from any non aromatic, aromatic or heteroaromatic group and any substituents on any R do not contain electron donating substituents, and n and m is determined by the respective valence and oxidation state of A and C.
2. A process as claimed in Claim 1, wherein the ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth, and nitrogen.
3. A process as claimed in Claim 2, wherein R^1 , R^2 , R^3 and R^4 are independently selected from aromatic, including hetero aromatic, groups of which two or more of R^1 , R^2 , R^3 and R^4 are substituted on the atom adjacent to the atom bound to A or C and any substituent is non-electron donating.
4. A process as claimed in Claim 2, wherein all of R^1 , R^2 , R^3 and R^4 have non-electron donating substituents on the atom adjacent to the atom bound to A and C.
5. A process as claimed in any one of claims 1 to 4, wherein any non-electron donating substituent is non-polar.
6. A process as claimed in any one of claims 1 to 5, wherein ethylene is contacted with the catalyst system at a pressure of more than 10 barg.

F469

7. A process as claimed in any one of claims 1 to 6, wherein B is selected from any one of a group comprising: organic linking groups containing a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl group; inorganic linking groups comprising single atom links; ionic links and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
8. A process as claimed in any one of claims 1 to 7, wherein B is selected to be a single atom spacer.
9. A process as claimed in any one of claims 1 to 8, wherein B is selected to be $-N(R^5)-$, wherein R^5 is hydrogen or selected from the groups consisting of alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxy, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.
10. A process as claimed in any one of claims 1 to 9, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
11. A process as claimed in any one of claims 1 to 10, wherein A and C is independently phosphorus or phosphorus oxidised by S or Se or N or O.
12. A process as claimed in any one of claims 1 to 9 and 11, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a methyl, ethyl, ethylenyl, propyl, propenyl, propynyl, butyl, cyclohexyl, 2-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, benzyl, phenyl, tolyl, xylyl, *o*-methylphenyl, *o*-ethylphenyl, *o*-isopropylphenyl, *o*-*t*-butylphenyl, cumyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl and dimethylhydrazyl group.

F469

13. A process as claimed in Claim 12, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising an *o*-methylphenyl, *o*-ethylphenyl, *o*-isopropylphenyl, *o*-*t*-butylphenyl, phenyl, tolyl, biphenyl, and naphthyl group.
14. A process as claimed in any one of claims 1 to 9 and 11 to 13 wherein the ligand is selected from any one of a group comprising: $(o\text{-ethylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-isopropylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-isopropylphenyl})_2$, $(o\text{-methylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-methylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-ethylphenyl})(\text{phenyl})$, $(o\text{-ethylphenyl})_2\text{PN}(\text{isopropyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-isopropyl})_2\text{PN}(\text{isopropyl})\text{P}(o\text{-isopropyl})_2$, $(o\text{-methyl})_2\text{PN}(\text{isopropyl})\text{P}(o\text{-methyl})_2$, $(o\text{-t-butylphenyl})_2\text{PN}(\text{methyl})\text{P}(o\text{-t-butylphenyl})_2$, $(o\text{-t-butylphenyl})_2\text{PN}(\text{isopropyl})\text{P}(o\text{-t-butylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(\text{pentyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(\text{phenyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(p\text{-methoxyphenyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(\text{benzyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(1\text{-cyclohexylethyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(2\text{-methylcyclohexyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(\text{cyclohexyl})\text{P}(o\text{-ethylphenyl})_2$, $(o\text{-ethylphenyl})_2\text{PN}(\text{allyl})\text{P}(o\text{-ethylphenyl})_2$, $(3\text{-ethyl-2-thiophenyl})_2\text{PN}(\text{methyl})\text{P}(3\text{-ethyl-2-thiophenyl})_2$, $(2\text{-ethyl-3-thiophenyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-ethyl-3-thiophenyl})_2$ and $(2\text{-ethyl-4-pyridyl})_2\text{PN}(\text{methyl})\text{P}(2\text{-ethyl-4-pyridyl})_2$.
15. A process as claimed in any one of the claims 1 to 14, which process includes the step of combining in any order a heteroatomic ligand with a transition metal compound and an activator.
16. A process as claimed in Claim 15, which includes the step of generating a heteroatomic coordination complex *in situ* from a transition metal compound and a heteroatomic ligand.
17. A process as claimed in any one of claims 1 to 16, which process includes the step of adding a pre-formed coordination complex, prepared using the heteroatomic ligand and the transition metal compound, to a reaction mixture containing an activator.

F469

18. A process as claimed in any one of the claims 1 to 17, wherein the transition metal is selected from any one of a group comprising chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
19. A process as claimed in any one of the claims 16 to 18, wherein the transition metal is chromium.
20. A process as claimed in Claim 15 or Claim 16, wherein the transition metal compound is selected from an inorganic or organic salt, a co-ordination or organometallic complex.
21. A process as claimed in Claim 20, wherein the transition metal compound is selected from any one of a group comprising chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.
22. A process as claimed in any one of claims 16 to 21, wherein the transition metal is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
23. A process as claimed in any one of claims 16 to 22, wherein the transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.01:100 to 10 000:1.
24. A process as claimed in Claim 23, wherein the transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.
25. A process as claimed in any one of claims 15 to 24, wherein the activator is selected from any one of a group consisting of organoaluminium compounds, organoboron compounds, organic salts, such as methyllithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

F469

26. A process as claimed in any one of claims 15 to 25, wherein the activator is selected from alkylaluminoxanes.
27. A process as claimed in Claim 26, wherein the alkylaluminoxane, or mixtures thereof, is selected from group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO).
28. A process as claimed in Claim 26 or Claim 27, wherein the transition metal from the transition metal compound and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1.
29. A process as claimed in Claim 28, wherein the transition metal compound and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.
30. A process as claimed in Claim 29, wherein the transition metal compound and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
31. A process as claimed in any one of claims 26 to 30, which includes the step of adding to the catalyst system a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of alkylaluminoxane.
32. A process as claimed in any one of claims 1 to 31, which includes the step of mixing the components of the catalyst system at any temperature between -20°C and 250°C in the presence of an olefin.
33. A process as claimed in Claim 32, wherein the temperature range is between 20°C and 100°C
34. A process as claimed in any one of the claims 1 to 33, wherein the process is carried out at temperatures in the range of 0-120 °C.

F469

35. A process as claimed in any one of the claims 1 to 33, wherein the process is carried out at a temperature range from 25-100°C.

36. A process as claimed in any one of the claims 1 to 35, which includes the step of contacting the olefin and the trimerisation product simultaneously with the trimerisation catalyst and a polymerisation catalyst so that co-polymerisation occur simultaneously leading to the incorporation of the trimerisation products into a copolymer.

37. A trimerisation catalyst system, which includes a transition metal compound and a heteroatomic ligand described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C and is selected to exclude $(CH_2)_xY(CH_2)_y$, where Y is $-P(R^6)-$, $-N(R^6)-$, $-As(R^6)-$, $-Sb(R^6)-$ or $-S-$ and x and y are individually 1-15 and wherein R^6 is hydrogen or a halogen or a nitro group or a hydrocarbyl or a substituted hydrocarbyl, and each R is independently selected from any non aromatic, aromatic or heteroaromatic group and any substituents on any R do not contain electron donating substituents, and n and m is determined by the respective valence and oxidation state of A and C.

38. A catalyst system as claimed in Claim 37, wherein the ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth, and nitrogen.

39. A catalyst system as claimed in Claim 38, wherein R^1 , R^2 , R^3 and R^4 are independently selected from aromatic, including hetero aromatic, groups of which two or more of R^1 , R^2 , R^3 and R^4 are substituted on the atom adjacent to the atom bound to A or C and any substituent is non-electron donating.

40. A catalyst system as claimed in Claim 37 wherein all of R^1 , R^2 , R^3 and R^4 have non-electron donating substituents on the atom adjacent to the atom bound to A and C.

F469

41. A catalyst system as claimed in any one of claims 37 to 40, wherein any non-electron donating substituent is non-polar.
42. A catalyst system as claimed in any one of claims 37 to 41, wherein B is selected from any one of a group comprising: organic linking groups containing a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl group; inorganic linking groups comprising single atom links; ionic links and a group comprising methylene, dimethylmethylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
43. A catalyst system as claimed in any one of claims 37 to 42, wherein B is selected to be a single atom spacer.
44. A catalyst system as claimed in any one of claims 37 to 43, wherein B is selected to be $-N(R^5)-$, wherein R^5 is hydrogen or selected from the groups consisting of alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.
45. A catalyst system as claimed in any one of claims 37 to 44, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
46. A catalyst system as claimed in any one of claims 37 to 45, wherein A and C is independently phosphorus or phosphorus oxidised by S or Se or N or O.
47. A catalyst system as claimed in any one of claims 37 to 44 and 46, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising a methyl, ethyl, ethylenyl, propyl, propenyl, propynyl, butyl, cyclohexyl, 2-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, benzyl, phenyl, tolyl, xylyl, o-methylphenyl, o-ethylphenyl, o-isopropylphenyl, cumyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl and dimethylhydrazyl group.

F469

48. A catalyst system as claimed in Claim 47, wherein R^1 , R^2 , R^3 and R^4 are independently selected from a group comprising an *o*-methylphenyl, *o*-ethylphenyl, *o*-isopropylphenyl phenyl, tolyl, biphenyl and naphthyl group.
49. A catalyst system as claimed in any one of claims 37 to 44 and 46 to 48 wherein the ligand is selected from any one of a group comprising: (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)₂, (*o*-isopropylphenyl)₂PN(methyl)P(*o*-isopropylphenyl)₂, (*o*-methylphenyl)₂PN(methyl)P(*o*-methylphenyl)₂, (*o*-ethylphenyl)₂PN(methyl)P(*o*-ethylphenyl)(phenyl), (*o*-ethylphenyl)₂PN(isopropyl)P(*o*-ethylphenyl)₂, (*o*-isopropyl)₂PN(isopropyl)P(*o*-isopropyl)₂, (*o*-methyl)₂PN(isopropyl)P(*o*-methyl)₂, (*o*-*t*-butylphenyl)₂PN(methyl)P(*o*-*t*-butylphenyl)₂, (*o*-*t*-butylphenyl)₂PN(isopropyl)P(*o*-*t*-butylphenyl)₂, (*o*-ethylphenyl)₂PN(pentyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(phenyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(*p*-methoxyphenyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(benzyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(1-cyclohexylethyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(2-methylcyclohexyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(cyclohexyl)P(*o*-ethylphenyl)₂, (*o*-ethylphenyl)₂PN(allyl)P(*o*-ethylphenyl)₂, (3-ethyl-2-thiophenyl)₂PN(methyl)P(3-ethyl-2-thiophenyl)₂, (2-ethyl-3-thiophenyl)₂PN(methyl)P(2-ethyl-3-thiophenyl)₂ and (2-ethyl-4-pyridyl)₂PN(methyl)P(2-ethyl-4-pyridyl)₂.
50. A catalyst system as claimed in any one of the claims 37 to 49, wherein the transition metal is selected from any one of a group comprising chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.
51. A catalyst system as claimed in any one of the claims 37 to 50, wherein the transition metal is chromium.
52. A catalyst system as claimed in Claim 50 or Claim 51, wherein the transition metal is derived from a transition metal compound selected from a group comprising of an inorganic salt, organic salt, a co-ordination complex and organometallic complex.
53. A catalyst system as claimed in Claim 52, wherein the transition metal compound is selected from a group comprising chromium trichloride tris-tetrahydrofuran complex,

F469

(benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.

54. A catalyst system as claimed in Claim 52 or Claim 53, wherein the transition metal compound is selected from a complex selected from chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.

55. A catalyst system as claimed in claims 52 to 54 wherein the transition metal compound and heteroatomic ligand have metal/ligand ratios from about 0.01:100 to 10 000:1.

56. A catalyst system as claimed in Claim 55, wherein the transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.

57. A catalyst system as claimed in any one of the claims 37 to 56, which includes an activator.

58. A catalyst system as claimed in Claim 57, wherein the activator is selected from any one of a group consisting of organoaluminium compounds, organoboron compounds, organic salts, such as methyllithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

59. A catalyst system as claimed in Claim 58, wherein the activator is selected from alkylaluminoxanes.

60. A catalyst system as claimed in Claim 59, wherein the alkylaluminoxane, or mixtures thereof, is selected from group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO).

61. A catalyst system as claimed in Claim 59 or Claim 60, wherein the transition metal compound and the aluminoxane are in such proportions relative to each other to provide Al/metal ratios from about 1:1 to 10 000:1.

F469

62. A catalyst system as claimed in Claim 61, wherein the transition metal compound and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.
63. A catalyst system as claimed in Claim 62, wherein the transition metal compound and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
64. A catalyst system as claimed in any one of claims 59 to 63, which includes a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of aluminoxane.
65. Use of a trimerisation catalyst system as claimed in any one of claims 37 to 64 for the tetramerisation of olefins.
66. Use of a trimerisation catalyst system as claimed in any one of claims 37 to 64 for the tetramerisation of ethylene.
67. Use of a ligand for a trimerisation process as claimed in any one of claims 1 to 36.
68. Use of a ligand for a trimerisation catalyst system as claimed in any one of claims 37 to 64.
69. An olefin trimerisation process substantially as described herein.
70. An olefin trimerisation catalyst system substantially as described herein.